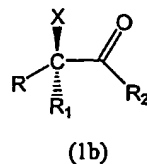
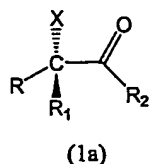
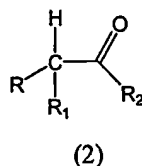


# Claims

1. A process for the catalytic asymmetric synthesis of an optically active compound of the formula (1a) or (1b)



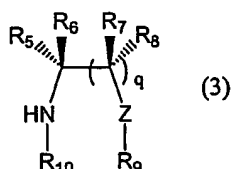
- 5 wherein R is an organic group; X is halogen; R<sub>1</sub> and R<sub>2</sub> which may be the same or different represents H, or an organic group or R<sub>1</sub> and R<sub>2</sub> may be bridged together forming part of a ring system; R and R<sub>2</sub> may be bridged together forming part of a ring system; with the proviso that R and R<sub>1</sub> are different and R<sub>2</sub> when different from H is attached through a carbon-carbon bond, comprising the step of reacting a compound of the formula
- 10 (2)



- 15 with a halogenating agent in the presence of a catalytic amount of a chiral nitrogen containing organic compound.

2. The process according to claim 1 wherein R<sub>2</sub> is H or an optionally substituted C<sub>1-10</sub> alkyl group or R and R<sub>2</sub> are bridged together forming part of a ring system.
3. The process according to claim 1 or 2 wherein R<sub>1</sub> is H or an optionally substituted C<sub>1-10</sub> alkyl group.
4. The process according to any of the preceding claims wherein R is an optionally substituted C<sub>1-10</sub> alkyl group, an optionally substituted C<sub>2-8</sub> alkylene group or a C<sub>1-3</sub>-alkylaryl group.
5. The process according to claim 4 wherein R is an optionally substituted C<sub>1-6</sub> alkyl group, an optionally substituted C<sub>2-4</sub> alkylene group or a C<sub>1-2</sub>-alkylaryl group.

6. The process according to claim 4 or 5 wherein  $R_1$  and  $R_2$  are H.
7. The process according to claim 1 wherein the chiral nitrogen containing organic compound is selected among compounds having a primary or secondary nitrogen atom or when appropriate in one of its salt forms.
8. The process according to claim 7 wherein the chiral nitrogen containing organic compound is selected among compounds of the formula (3)



wherein  $q$  is 0 or 1;

$R_5, R_6, R_7, R_8$ , which may be the same or different represents H, alkyl, haloalkyl, alkoxy, OH, amino, amide, silyl, silyl ether,  $\text{COR}_{11}$ , optionally substituted aryl, an optionally substituted heterocycle, alkyl substituted with at least one OH group, an optionally substituted amino group or optionally substituted aryl or heterocycle or  $R_5$  and  $R_6$  together or  $R_7$  and  $R_8$  together may represent a carbonyl group or when  $q$  is 1,  $R_5$  with either  $R_7$  or  $R_8$  may be bridged together forming part of a ring system;  $R_{11}$  represents an optionally substituted amino group or  $\text{OR}_{12}$  wherein  $R_{12}$  represents H, alkyl or phenyl;

$R_9$  and  $R_{10}$ , which may the same or different represents H, alkyl, OH, or alkoxy; or  $R_9$  and  $R_{10}$  may be bridged together forming part of a ring system;

$Z$  is S, O,  $\text{C}=\text{O}$ ,  $\text{C}(\text{R}_{14})_2$ ,  $\text{N}-\text{R}_{14}$  wherein  $R_{14}$  is  $R_5$ ;

with the proviso that the groups  $R_5, R_6, R_7, R_8, R_9, R_{10}, R_{14}$ , and  $Z$  are selected so that the compound (3) is a chiral compound.

9. The process according to claim 8 wherein  $q$  is 1;  $R_5, R_6, R_7, R_8$  which may the same or different represents H,  $\text{COR}_{11}$ , optionally substituted aryl or methyl substituted with at least one of the following, an OH group, an optionally substituted amino group or an optionally substituted aryl or heterocycle group; or  $R_5$  and  $R_7$  together represents a  $\text{C}_{3-5}$

alkylene bridge;

R<sub>11</sub> represents OH, NH<sub>2</sub> or NH-alkyl;

R<sub>9</sub> and R<sub>10</sub> are H or R<sub>9</sub> and R<sub>10</sub> together represents a methylene bridge optionally substituted with phenyl, benzyl, COOH or CO-alkoxy;

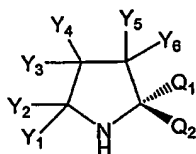
5 Z is CH-R<sub>14</sub> or N-R<sub>14</sub> wherein R<sub>14</sub> represents H or alkyl.

10. The process according to claim 9 wherein either R<sub>5</sub> or R<sub>6</sub> represents H; R<sub>7</sub> and R<sub>8</sub> represents H; R<sub>9</sub> and R<sub>10</sub> together represents a methylene bridge and Z is CH<sub>2</sub>.

10 11. The process according to claim 3 wherein R<sub>1</sub> is H and R and R<sub>2</sub> each represents an optionally substituted C<sub>1-10</sub> alkyl group or R<sub>2</sub> together with R forms an optionally substituted C<sub>3-5</sub>-alkylene bridge optionally with one or more of the carbon atoms being replaced by a heteroatom.

15 12. The process according to claim 1 wherein one or more acids are added to the reaction media.

13. The process according to claim 8, wherein the compound of formula (3) is a compound of formula (4)



(4)

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wherein Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub>, Y<sub>4</sub>, Y<sub>5</sub>, Y<sub>6</sub> which may be the same or different represents H, an alkyl, haloalkyl, an aryl, an alkylaryl, a heterocycle, a halogen, a hydroxyl, a carbonyl, an alkoxy, an ester, an amine, an amide, a silyl, a silyl ether, or Y<sub>2</sub> and Y<sub>3</sub> or Y<sub>4</sub> and Y<sub>5</sub> may be bridged together forming part of a ring system one of Q<sub>1</sub> and Q<sub>2</sub> represent H, alkyl, haloalkyl, alkylaryl and the other the group CY<sub>7</sub>Y<sub>8</sub>(OY<sub>9</sub>) wherein Y<sub>7</sub> and Y<sub>8</sub> which may be the same or different represents alkyl, haloalkyl, an alkylaryl, a heterocycle, or optionally substituted aryl and Y<sub>9</sub> represents a silyl group.

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14. A compound of the formula (4) as disclosed in claim 13.

15. The compound according to claim 14, wherein Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub>, Y<sub>4</sub>, Y<sub>5</sub>, Y<sub>6</sub> each represents H; one of Q<sub>1</sub> and Q<sub>2</sub> represents H; Y<sub>7</sub> and Y<sub>8</sub> each represents an optionally substituted aryl group, wherein the substituents are selected among alkyl and haloalkyl; Y<sub>9</sub> represents tri-alkyl silyl.

16. The compound according to claim 15, wherein Y<sub>7</sub> and Y<sub>8</sub> each represents 3,5-di-trifluoromethyl phenyl and Y<sub>9</sub> represents trimethyl silyl.

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17. The compound according to claim 15, wherein Y<sub>7</sub> and Y<sub>8</sub> each represents 3,5-di-methyl phenyl and Y<sub>9</sub> represents trimethyl silyl.